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Unified Science Associates, Inc.  
826 South Arroyo Parkway  
Pasadena, California 91105  
213-681-3486

THIRD QUARTERLY REPORT  
2-1-67 through 4-30-67

Prepared for  
NATIONAL AERONAUTICS AND  
SPACE ADMINISTRATION

Under CONTRACT NAS 7-437  
GASEOUS ELECTROLYTES FOR  
BATTERIES AND FUEL CELLS

S. Naiditch  
Principal Investigator

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## ABSTRACT

The main effort this quarter was directed toward finding differences in the behavior of the electrode-electrolyte interface for liquid and gaseous electrolytes. Earlier, we had established that there were no differences in emfs of amalgam concentration cells. For this reason we turned to the process of electrodeposition as a tool to see whether important differences would show up under dynamic conditions. Our expectation was that deposition out of dense gaseous electrolytes would be more continuous and the deposits more crystalline and less spongy than out of liquid electrolytes. This was based on the picture that any gas produced during electrolysis would not be constrained to the surface region as a bubble since the gaseous electrolyte should not have the surface tension of a liquid electrolyte. Experimental results to date indicate that the differences are indeed major and that, as a by-product, it may be practical to produce single crystal whiskers out of the dense gaseous electrolyte.

In the first run of this period (E8), silver electrodeposit out of the liquid state ( $-70^{\circ}$ ,  $15^{\circ}$ ,  $103^{\circ}\text{C}$ ) became increasingly sparkly or crystalline in appearance as the critical temperature was approached. In the supercritical region ( $140^{\circ}\text{C}$ ), the deposit on the bulk of the substrate was much more sparkly or crystalline in appearance. At the tip of the cathode, filaments were observed which were presumably single crystal silver (Fig. 2).

In the third run, cuprous chloride was electrolyzed at  $23^{\circ}\text{C}$  and  $144^{\circ}\text{C}$  with mixed success (Cell E12). Although deposits were obtained, experimental

conditions were apparently not satisfactory for a metallic deposition. For the time being experiments with cuprous chloride have been discontinued.

Silver was deposited in the run with Cell E16. The deposit out of the dense gaseous electrolyte ( $142^{\circ}\text{C}$ ) was distinctly different from that out of the liquid electrolyte ( $21^{\circ}\text{C}$ ). The low temperature deposit was frosty in appearance whereas that out of the dense gaseous electrolyte was quite sparkly or crystalline in appearance. In addition, long filaments grew on one electrode. Unfortunately this growth broke but the separate pieces were from  $1/16''$  to  $1/8''$  long.

In the next run (Cell E13), silver was deposited on three different cathodes at  $140^{\circ}\text{C}$ . On two electrodes the deposits were metallic and somewhat crystalline in appearance; on the third, whiskers were produced. They apparently broke off the electrode and were lying loose in the cell when the cell was removed from the bomb. There were several whiskers of length up to 5 mm (Fig. 3).

In Cell E14, several types of silver deposits were produced out of the dense gaseous electrolyte ( $140^{\circ}$  to  $141^{\circ}\text{C}$ ). One was metallic and somewhat crystalline and whiskery in appearance. Another was in rather long trees. The main shaft of one tree was about 6.5 mm long (Fig. 4). The branches on this tree were relatively short. It may well be that the branches are merely growth on the side faces of a single crystal filament. Twinning appears to have occurred in at least two places.

Because of the interesting results on the deposition of silver from dense gaseous  $\text{AgNO}_3\text{-NH}_3$  and because the total resistance of the cell is sometimes lower in the dense gaseous state than in the liquid state at room temperature, it appeared desirable to examine the conductivity of  $\text{AgNO}_3\text{-NH}_3$ . Two cells were built and filled and readings initiated on one cell. The concentration of solute in the two cells in the gas phase will be almost identical whereas the density of ammonia will be 12% higher in one cell. One interesting feature of the dense gaseous medium is that both solvent and solute densities can be varied independently of each other whereas in the liquid state only the solute density can be varied at a given temperature.

The applicability of polarography to the study of dense gaseous electrolytes is reviewed. A new type of polarographic cell is designed to be used with these electrolytes. Preliminary experiments have been made to check out the system as well as the design of the cell. Construction of the new cell should be completed shortly.

## I. INTRODUCTION

The work during the past quarter has been concerned mainly with the electro-deposition experiments. These experiments are being carried out to establish differences in dynamic electrochemical properties of liquid and gaseous electrolytes. In addition, there has been considerable preparatory work done in setting up a dropping mercury electrode polarography experiment. This experiment is expected to furnish information about species present, diffusion processes, and conditions at the electrode surface in a gaseous electrolyte. Finally, two conductivity cells have been designed and built for the purpose of measuring the conductivity of  $\text{AgNO}_3$  in  $\text{NH}_3$  as a function of temperature over the range between room temperature and temperatures well above the critical point of  $\text{NH}_3$ . These cells have been filled with the electrolyte and conductivity measurements begun on one of them.

## 2. ELECTRODEPOSITION EXPERIMENTS

During this quarterly period 10 electrodeposition cells have been built and filled. Six of these were run successfully, producing some very interesting results, while the remaining four were broken, either in filling or during attempted experiments before useful data could be obtained. The cells were numbered E7 to E16, inclusive, and were of the general type shown in Fig. 1.

A summary of these experiments is as follows.

<u>Cell No.</u>	<u>Electrodes</u>	<u>Salt</u>	<u>Result</u>
E7	6-Pt-Half-length cathodes	CuCl	Broken during filling.
E8	Same	AgNO <sub>3</sub>	Whiskers - photographed.
E9	6-Pt-Very small cathodes	AgNO <sub>3</sub>	Spongy deposits
E10	Same	CuCl	No visible deposit obtained
E11	4-Pt-Long, Med., Small cathodes	AgNO <sub>3</sub>	Broken during experiment
E12	Same	CuCl	Non-metallic, red deposit
E13	Same	AgNO <sub>3</sub>	Long whiskers - photographed
E14	Same	AgNO <sub>3</sub>	Long feathers - photographed
E15	Same	AgNO <sub>3</sub>	Broken during experiment
E16	Same	AgNO <sub>3</sub>	Long whiskers

Detailed accounts of the successful experiments follow. They are arranged in the chronological order in which they were performed.

## 2.1 CELL E8

This cell (whose volume was approximately 40 cc) was filled with 0.1572 gm  $\text{AgNO}_3$  in about 20 cc of  $\text{NH}_3$  at  $-78^\circ\text{C}$ . The cell had six 0.016" diam. Pt. wire electrodes. One of these was 2" long and was used as the anode. The other five were 1.25" long and were used as cathodes. Two of the cathodes were used for low temperature electrodeposition prior to placing the cell in the bomb while the remaining three were used at high temperatures. The two low temperature cathodes were designated Gn and Gy while the anode was designated A and the three high temperature cathodes were B, C and D.

The experimental conditions were as follows.

<u>Cathode</u>	<u>Temp.</u> <u><math>^\circ\text{C}</math></u>	<u>Cell</u> <u>Volts</u>	<u>Current</u> <u>ma.</u>	<u>Time</u> <u>Sec</u>	<u>Charge</u> <u>Faradays</u>
Gn	-70	3.6	10	60	$6.2 \times 10^{-6}$
Gy	-70	1.5	1	810	$8.4 \times 10^{-6}$
C	15	0.7	1	615	$6.4 \times 10^{-6}$
B	103	0.7	1	660	$6.8 \times 10^{-6}$
D	140	0.5	1	690	$7.15 \times 10^{-6}$

The low temperature deposits were examined immediately after deposition and were observed to be black and fluffy in appearance, particularly the deposit on Gn which was about 0.5 mm thick. Pieces of this deposit were observed to break off and drift about in the liquid ammonia, indicating fragility and low density. The deposit on Gy was much thinner and stronger, but was also black and non-metallic in appearance.

After the high temperature electrodepositions out of the dense gaseous electrolyte, the cell was removed from the bomb intact. Half the  $\text{NH}_3$  was missing, indicating that there was a slow leak. Both of the low temperature deposits were considerably reduced in size. A black powder which could be wiped off remained on Gn while a thin black crust which could be scraped off in small pieces remained on Gy. This crust appeared metallic on its inner side while the outer side appeared non-metallic.

The three higher temperature deposits were all metallic in appearance. The deposit at  $15^\circ\text{C}$  on C was metallic and fairly smooth in appearance. That at  $103^\circ\text{C}$  on B was metallic and somewhat sparkly or crystalline in appearance. The deposit on D at  $140^\circ\text{C}$  was very sparkly or crystalline in appearance. On the pointed tip of cathode D, sharp projections, presumably single silver crystals or whiskers, were observed. These were photographed and a copy of the photograph is shown in Fig. 2. Under the microscope the crystals appear to be three-sided. The sides are apparently planar and give spectral reflection of light.

Another interesting feature is the increase in conductivity of the cell with increasing temperature. This can be seen by comparing the voltages required to pass a current of 1 ma between anode A and cathodes Gn, B, C and D. The required voltage drops from 1.5 to 0.5 as the temperature increases from  $-70^\circ\text{C}$  to  $+140^\circ\text{C}$ , indicating an increase in apparent cell conductivity by a factor of 3. This is surprising in view of our previous experiments in which the cell conductivity decreased, in one case by a

factor of 400. It may be that this behavior is due to variation in electrolyte density due to variations in cell filling. High conductivities are needed for practical utilization of dense gaseous electrolytes for energy conversion. Since there may be conditions under which it may be possible to produce high conductivities near the critical point itself, i.e., in the least stringent portion of the supercritical region, this feature will be examined further. It is therefore planned to make four-probe measurements of the conductivities of  $\text{AgNO}_3$  in  $\text{NH}_3$  solutions as a function of temperature, density, and concentration. Two cells have been prepared and filled for these measurements and the conductivity measurements will be made in the next quarter.

## 2.2 CELL E9

This cell (of 40 cc volume) was filled with 0.1679 gm  $\text{AgNO}_3$  in about 25 cc of  $\text{NH}_3$  at  $-78^\circ\text{C}$ . The cell had six electrodes, one being a 0.016" diam. by 2" long Pt wire used as the anode while the other five were 0.016" diam. Pt wires covered with glass for a short distance and cut off flush with the glass to leave exposed a 0.016" diam. circular area for the electrode surface. Two of the cathodes (designated Gn and Gy) were used for low temperature electrodeposition while the other three (B, C and D) were used at high temperature. Cathodes B and D were brought in through the top of the cell while the anode A and cathodes Gn, Gy, and C were brought in through the bottom.

<u>Cathode</u>	<u>Temp.</u> <u><math>^\circ\text{C}</math></u>	<u>Cell</u> <u>Volts</u>	<u>Current</u> <u>ma.</u>	<u>Time</u> <u>Sec.</u>	<u>Charge</u> <u>Faradays</u>
Gn	-60	2.5	0.3	20	$6.2 \times 10^{-7}$
Gy	-60	1.4	0.03	400	$1.24 \times 10^{-6}$
C	140	0.1	0.01	720	$7.5 \times 10^{-7}$
B	150	380	0.003	8400	$2.6 \times 10^{-6}$
D	150	380	0.01	600	$6.2 \times 10^{-7}$

The deposits on Gn and Gy were in the form of fluffy black hemispheres which disappeared during the high temperature experiments leaving behind a thick crust which was metallic and spongy in appearance. A very similar deposit was found on C. In fact there was no marked difference in the appearance of these three deposits. When prodded with a sharp instrument

under the microscope, the deposits on Gn and Gy were found to be resilient and quite spongy in character while that on C was very brittle.

No deposits were observed on B and D. During the electrodeposition on C at 140°C, the impedance between A and cathodes B and D was observed to be very high, suggesting that B and D were not immersed in the electrolyte. This situation persisted at 150°C, which should have been well above the critical point. It is therefore suspected that the cell had broken at the top and that the top portion of the cell contained nitrogen from the external pressure system rather than electrolyte. After the attempted deposition on D had been concluded, it was found that the impedance between A and C had also become very large. When removed from the bomb, the cell was found broken open at the top.

### 2.3 CELL E12

This cell, of 34 cc volume, was filled with 0.0611 gm of CuCl in 17 cc of  $\text{NH}_3$  at  $-78^\circ\text{C}$ . The cell had four 0.020" diam. Pt wire electrodes, designated A, B, C and D. The anode A and the cathode B were 1.75" long, the cathode D was 1.13" long and the cathode C was cut off flush with the glass covering the feedthrough so that only a 0.020" diam. circular surface was exposed as the electrode surface. Most of the CuCl did not dissolve in the liquid  $\text{NH}_3$ . The solution had a light blue tint. The electrodeposition conditions were as follows:

<u>Cathode</u>	<u>Temp.</u> <u><math>^\circ\text{C}</math></u>	<u>Cell</u> <u>Volts</u>	<u>Current</u> <u>ma.</u>	<u>Time</u> <u>Sec.</u>	<u>Charge</u> <u>Faradays</u>
D	23	1.75	1.0	600	$6.21 \times 10^{-7}$
B	144	300 to 14	$\sim 1.0$	660	$\sim 7 \times 10^{-7}$
C	144	10	0.01	6015	$6.23 \times 10^{-8}$

The current during the low temperature deposition on cathode D was quite steady. This deposition was performed before the cell had been heated to the higher temperature. The deposit on D had no metallic lustre; was black to dark copper in color; and had a soft, powdery consistency. After the run, it could be easily scraped off to leave a blue-black electrode surface near the longer end, changing to silvery near the upper end. The density of the deposit was fairly uniform as a function of height over all but the last 1/8" of the wire. This wire apparently extended out of the liquid and was covered only with a very light deposit. The deposit was thicker, however, on the side of the wire away from the anode. Some coppery powder also extended onto the feedthrough glass.

At 144°C, the current fluctuated at constant cell voltage, sometimes by an order of magnitude and in the case of cathode B, tended to rise to such an extent that the applied voltage across cell had to be dropped from 300 to 14 volts by the end of the experiment in order to maintain the average current near 1 ma. The current was much steadier on cathode C although there were a few fluctuations.

The deposit on most of electrode B was very similar to that on D, with the exception of a marked decrease in density with height along the upper half of the electrode wires. The density over the lower half appeared uniform.

There was one interesting feature on cathode B in the form of a thin, wire-like stem with a round lump on the end protruding from the side of the electrode. The length of this feature was about 0.02" with the diameter of the round lump being about 0.003" and the thickness of the stem being about 0.0005" to 0.001". The object had a dark coppery color without metallic lustre. It was fairly hard; the stem being flexible but not springy. It was apparently a growth of copper.

There was very little deposit on cathode C. Its surface was of copper color and there was copper-colored powder on the feedthrough glass.

The powdery character of the deposits from both liquid and gaseous electrolytes and the thinning of the deposits on the side of the cathode near the anode suggests that the current density was much too high. Since it is not practical to use a much lower current density in the present type of experiment, we are discontinuing the use of CuCl.

#### 2.4 CELL E16

This cell, of 37 cc volume, was filled with 0.1085 gm of  $\text{AgNO}_3$  in 19 cc of  $\text{NH}_3$  at  $-78^\circ\text{C}$ . The electrodes were as in Cell E12. During the sealoff operation, after filling with  $\text{NH}_3$ , a small amount of air may have gotten into the cell. The experimental conditions were as follows:

<u>Cathode</u>	<u>Temp °C</u>	<u>Cell Volts</u>	<u>Current ma.</u>	<u>Time Sec.</u>	<u>Charge Faradays</u>
D	21	0.78	1.0	900	$9.32 \times 10^{-7}$
B	142	0.83 to 0.9	1.0	1320	$1.37 \times 10^{-6}$
C	142	0.46	0.095(av)	3615	$2.7 \times 10^{-7}$

Cathode C was maintained at constant potential and the current allowed to increase as the deposition of silver increased the surface area of the electrode. The current increased with time in a nonlinear manner from 0.06 ma to 0.130 ma, indicating that the deposition of silver had approximately doubled the surface area. The cell broke during cooling after the experiment.

The low temperature deposit on D appeared quite smooth and clean. The deposit appeared metallic although the surface did not give specular reflection, indicating a slight roughness on the surface. The deposit was quite uniform in appearance over the entire electrode surface.

The deposit on B appeared clean, metallic, and quite sparkly or crystalline in appearance. The deposit did not appear to be very thick and did not cover the entire electrode surface but was in the form of small, sparkly

dots quite closely spaced but between which the Pt electrode surface could still be seen. There was a density gradient along the upper 1/2" of the electrode wire with the deposit becoming quite thin near the top and no whiskers had grown from the top of the wire. The density gradient and lack of whiskers on the long electrode are quite different from the results obtained earlier with cell E8.

The deposit on C was in the form of a thick, crystalline metallic crust with several protuberances. Some of these exhibited fairly large reflecting faces. At first it was thought that this was all that had been deposited on C. The increase in electrode area due to the deposit was much smaller than expected from the observed decrease in cell impedance. Later, several whiskers were found in the deep cup at the bottom of the cell where electrode C was brought into the cell (see fig. 1). These whiskers were much larger than those from E8, being 1/16" to 1/8" long. They had presumably fallen from the electrode either when the cell burst during cooling or when the cell was being removed from the bomb. The whiskers stuck in the bottom of the cup and attempts to remove them resulted in their loss. Larger whiskers have been recovered from subsequent experiments.

## 2.5 CELL E13

This cell, of 35 cc volume was filled with 0.0993 gm of  $\text{AgNO}_3$  in 18 cc of  $\text{NH}_3$  at  $-78^\circ\text{C}$ . The electrodes were as in cell E12. The cell had no freeze cup. The experimental conditions were as follows:

<u>Cathode</u>	<u>Temp.</u> <u><math>^\circ\text{C}</math></u>	<u>Cell</u> <u>Volts</u>	<u>Current</u> <u>ma.</u>	<u>Time</u> <u>Sec.</u>	<u>Charge</u> <u>Faradays</u>
B	140	1.2	2.0	660	$1.37 \times 10^{-6}$
D	140	0.97	1.0	600	$6.2 \times 10^{-7}$
C	140	1.05	0.453(av)	4800	$2.25 \times 10^{-6}$

The voltage on electrode C was held constant while the current was allowed to vary as the deposit grew. Because of the small size of cathode C, the growth of the deposit caused a marked increase in current with time, so that the current increased from 0.1 ma at the beginning of the experiment to 0.7 ma near the end. The current was recorded as a function of time and the time averaged result is given above.

The deposits on B and D were both metallic and somewhat crystalline in appearance when viewed under the microscope. Unlike the case of cell E8, there were no whiskers growing from the tips of these electrodes. The deposit on C was very crystalline and hairy in appearance and extended for some distance over the surface of the glass. In addition, there were several whiskers of length up to 5 mm. These had apparently broken off from electrode C and were lying loose in the cell. Photographs were taken of the deposits and of the whiskers. A photograph of some of the whiskers

is shown in Fig. 3. The great increase in size of the whiskers over those from cell E8 gives encouragement to the hope that large, single crystals can be grown from gaseous electrolytes.

The lack of small whiskers on B and D and the rather rough character of the whiskers obtained from C may indicate the presence of impurities which were avoided on cell E8 by using a freeze valve during the sealoff operation. Consequently, freeze valves will be used in the next series of electro-deposition experiments.

## 2.6 CELL E14

This cell, of about 35 cc volume, was filled with 0.0968 gm of  $\text{AgNO}_3$  in 17 cc of  $\text{NH}_3$  at  $-78^\circ\text{C}$ . The cell had electrodes similar to those of cells E10 and E13 and like E13 had no freeze cup. The conditions during electro-deposition were as follows.

<u>Electrodes</u>	<u>Temp.</u> <u><math>^\circ\text{C}</math></u>	<u>Cell</u> <u>Volts</u>	<u>Current</u> <u>ma.</u>	<u>Time</u> <u>Sec.</u>	<u>Charge</u> <u>Faradays</u>
$\text{A}^+\text{B}^-$	140	0.85	2.0	600	$1.24 \times 10^{-5}$
$\text{D}^+\text{B}^-$	141	0.85	1.17	630	$7.6 \times 10^{-6}$
$\text{A}^+\text{C}^-$	141	0.85	0.466(av)	5100	$2.5 \times 10^{-5}$
$\text{A}^+\text{D}^-$	141	0.85	1.4	600	$8.7 \times 10^{-6}$

The second run ( $\text{B}^-\text{D}^+$ ) was done in error, the anode wire having been switched from A to D after the first run rather than the cathode being switched from B to D as had been intended. The same voltage was applied across the cell in all experiments. In the case of cathode C, the voltage was held constant while the current was allowed to vary as the deposit grew. The current was recorded as a function of time and the time average is given in the above table. The current increased from 0.27 ma to 0.58 ma during the course of the experiment.

It was thought that the error made in the second run in which an additional deposit was made on B using D rather than A as the anode would surely increase the thickness of the deposit on B and possibly contaminate the surface of electrode D. The deposit on B, however, was found to be quite different

than expected. The bottom half of the electrode was covered with a fairly clean metallic deposit with a sparkly or crystalline and somewhat whiskery appearance. The deposit on the upper part, however, while somewhat metallic in appearance, was lumpy, and wrinkled, being apparently much thicker than on the lower part. The transition between the lower and upper portions was uniform, the deposit becoming thicker, lumpier and more wrinkled toward the upper end of the electrode.

The deposit on D, on the other hand, was cleaner than on B and very sparse. There was almost no deposit near the top of the electrode while the remainder was apparently in the form of very tiny whiskers growing from the bare Pt surface.

The deposit on C was stubbly and crystalline in appearance. It had some metallic lustre but did not appear too clean. In addition, there were several very small trees growing from the electrode. In the cup on the bottom of the cell beneath electrode C there were several tree fragments including one about 6.5 mm long. These had apparently broken from C, giving the stubbly appearance. A photograph of the largest fragment is shown in Fig. 4. This deposit is in the shape of rather long tree. There appear to be three points on its length where twinning occurred. The branches on this tree are relatively short. It may well be that the branches are merely growths on the side faces of a single crystal filament.

## 2.7 CONCLUSIONS

The principal objective of this particular series of experiments has been achieved, namely, we have shown that electrodeposition out of dense gaseous electrolytes is markedly different than out of liquid electrolytes. In addition, we feel that we have demonstrated the feasibility of growing single crystals and/or single crystal filaments out of dense gaseous electrolytes once the proper conditions are found.

At the beginning of this particular series of experiments, we had shown that there the emfs of amalgam concentration cells did not depend on the state of the electrolyte, i.e., whether liquid or dense gaseous. We then turned to the question of what kinds of differences in properties should show up. One of the differences we anticipated is that under dynamic electrolytic conditions, gases such as hydrogen which form on electroreduction should diffuse away from the neighborhood of the electrode once they are desorbed. In contrast, in the case of liquid electrolytes, the surface tension of the liquid constrains the gases as bubbles to the region of the surface. Hence, we predicted that electrodeposits out of dense gaseous electrolytes would be more crystalline in appearance and less pock marked than those out of the liquid state under comparable conditions. This reasonable picture is in accord with the results of the experiments which were guided by this hypothesis.

The experiments in the next section on polarography are being undertaken to uncover some more of the differences in properties between the two electrolyte states. This work will be discussed further in the next section.

### 3. CONDUCTIVITY EXPERIMENT

Because of the interesting results obtained on the deposition of silver from dense gaseous  $\text{AgNO}_3\text{-NH}_3$ , and because the total resistance of the cell was sometimes lower in the dense gaseous state ( $140^\circ\text{C}$ ) than in the liquid state ( $25^\circ\text{C}$ ), it appeared desirable to examine the conductivity behavior of  $\text{AgNO}_3\text{-NH}_3$ .

There has been a considerable variation between cells in the apparent gaseous conductivity while the apparent liquid conductivity has been very similar. This suggests that the gaseous state may be very sensitive to small differences in concentration and electrolyte density, as would be suggested by the results of Copeland et al on the dielectric constant of dense gaseous water. In order to make definitive measurements of these effects, two conductivity cells were designed and built, having four electrodes of coiled 0.10" diam. silver wire (Fig. 5). These cells were quite similar to previous conductivity cells, being designed for four probe conductivity measurements, in which the measuring electrodes draw no current, and having geometrically determined cell constants.

Two cells (designated C1 and C2) have been built and filled with  $\text{AgNO}_3\text{-NH}_3$  solutions at concentrations of 0.0345 and 0.040 moles/liter at  $-78^\circ\text{C}$  respectively. The solutions occupied 56.2% and 50.2% of the cells at  $-78^\circ\text{C}$ , giving rise to a molar volume of ammonia in the gas phase of 41.5 cc and 46.3 cc, respectively. If all of the salts remain in solution in the dense gaseous  $\text{NH}_3$ , then in the gas phase the concentrations of  $\text{AgNO}_3$  will

be almost identical while in cell C1 the density of ammonia will be 12% higher than in cell C2.

One of the interesting potentials of the dense gaseous medium is the above feature that both solute and solvent densities can be varied independently, unlike the case of the liquid state, where only the solute density can be varied at a given temperature.

Cell C2 had been loaded into the bomb and readings were being taken at the end of this report period. Electrode emf and electrolyte conductivity measurements were being made at 10°C intervals allowing two hours for equilibration after changing temperature. Measurements had been taken over the range from 18° to 98°C by the end of the report period. These measurements indicate that the electrodes are fairly well behaved and that good conductivity measurements can be obtained. The detailed results will be given in the next report when the measurements will have been completed.

#### 4. POLAROGRAPHY EXPERIMENT

##### 4.1 Background - Polarography in General

Voltammetry is the branch of electrochemistry that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. The dropping mercury electrode consists of a very fine glass capillary with one end connected to a mercury reservoir while the other is immersed in the solution being investigated. Mercury flows through the capillary causing a drop to grow on the end of the capillary and then fall. As soon as one drop falls, another begins to form. Each drop exactly duplicates its predecessor so that the currents are reproducible from one drop to the next. Also, solid products cannot accumulate on the electrode surface which could change its properties. With a dropping electrode, a momentary shock or vibration will cause one drop to behave erratically whereas with a stationary electrode the whole measurement can be ruined by changing the structure of the diffusion layer which is slowly growing away from the electrode surface.

A polarographic cell contains the solution to be measured, the dropping mercury electrode (DME) and a reference electrode against which the potential of the DME is established. Because of the very large surface area of the reference electrode and the low currents involved, the reference electrode, which also serves as the counter electrode, does not polarize. To investigate a metal ion in the solution the potential of the DME is varied from zero towards negative values. If only one cation is present, the current will

remain constant until the potential of the DME is sufficiently negative to reduce the cation. At this point the current increases rapidly as the DME becomes more negative until all of the cations which diffuse to the DME are reduced on its surface. From this point, as the DME is made still more negative, the current remains constant and is limited by the rate at which the cations can diffuse to the DME. Anions produce similar results when the DME is made positive.

#### 4.2 Background - Applicability of Polarography to Dense Gaseous Electrolytes

For each ionic species present, including different solvation states of the same ion, there is a characteristic potential above which (in the absolute sense) it will be oxidized or reduced, as the case may be, and below which it will not. It is thus possible to identify the species present in a solution, including different solvation states of the same ion. From a measurement of diffusion limited current for a particular species it is possible to obtain the diffusion constant for that species if the concentration is known; or the concentration if the diffusion constant is known.

Finally, even when no ions are being oxidized or reduced at the DME, a small current flows. Because no ions are being oxidized or reduced on the DME, there is effectively an insulating layer between the mercury drop and the surrounding electrolyte. The voltage applied to the cell occurs across this layer which is called the electrical double layer. The mercury drop and surrounding electrolyte thus form the two plates of a capacitor. As the mercury drop grows, the capacitance increases, requiring a current to flow to maintain same voltage across it. This is the residual current. From a measurement of the residual current, the differential capacity of the electrical double layer can be obtained, which can be interpreted in terms of conditions at the surface of the DME. Thus a polarographic experiment can identify the ionic species present, including different solvation states of the same ion, give the diffusion constant or the concentration of each species, depending upon which is known, and give information about the electrical double layer at the electrode surface. Such information, if obtained with the electrolyte in the gaseous state, would be extremely interesting and pertinent to the present program.

#### 4.3 Status

In preparation for the proposed polarography experiments, a new type of polarographic cell has been designed to be used with dense gaseous electrolytes, and preliminary experiments have been performed. A recording polarograph is used to vary the potential between the reference electrode and the DME at a constant rate between desired initial and final points while recording the current through the cell. A schematic of the electrical circuit for this device is shown in Fig. 6. In addition to the voltage sweep and current measuring and recording sections, it contains a circuit to compensate for voltage drops across the current sensing resistor and the internal resistance of the cell and an integrating circuit to provide a desired amount of damping of the current swings produced by the DME. As each drop falls, the current drops practically to zero and then increases to its maximum as the next drop grows. It is usually desirable to average these swings to some extent. The present device uses flashlight cells to obtain the necessary voltages while a clock motor drives the gauged voltage dividing potentiometers for the voltage sweep and internal resistance compensator. The voltage across the current sensing resistor is recorded on a Baush and Lomb VOM 5 recorder, having a sensitivity of 10 mv full scale and an input resistance in excess of 10 megohms. The cell voltage can be swept through any desired amount between 0 and 4.5 V in a time of 8 minutes while the initial voltage can be set anywhere between  $\pm 1.5$  V. Current can be measured over the range from 0.5  $\mu$ a to 100  $\mu$ a, and the integration time can be set at 0, 2, 4, 8 and 20 seconds.

One of the problems associated with building a polarographic cell is to obtain a capillary which delivers drops at the proper rate. The optimum drop time is about 6 seconds and considerable experimentation was done in drawing down 1/2 mm capillary to obtain the desired drop time. When a suitable capillary had been obtained, a simple polarography experiment with an aqueous solution was carried out with good results. This experiment detected oxygen from air dissolved in 0.1 N aqueous KCl solution and duplicated published results. Another problem is to find a suitable reference electrode for use in ammonia. If chloride solutions are used, then a principal requirement is that the chloride salt of the reference electrode material should be insoluble in ammonia. Lead, cadmium, and zinc appear suitable on this basis. A polarographic cell for use with a gaseous electrolyte consisting of a chloride salt in  $\text{NH}_3$  has been designed around one of the capillaries that had suitable characteristics. Lead wire was chosen for the reference electrode. Construction should be completed shortly.

## 5. FUTURE PLANS

It is planned to continue the electrodeposition experiments with precautions to insure the purity of the electrolyte. Some of the platinum electrodes will be etched to expose the crystal surfaces to see if this encourages the growth of silver crystals on the platinum substrate. Vacuum melted silver drops will also be tried as electrodes. It is planned to continue the conductivity experiments with  $\text{AgNO}_3/\text{NH}_3$  in order to establish the dependence of concentration and density as well as temperature on the conductivity of a gaseous electrolyte. Finally, it is planned to perform polarographic experiments in gaseous chloride-ammonia solutions.

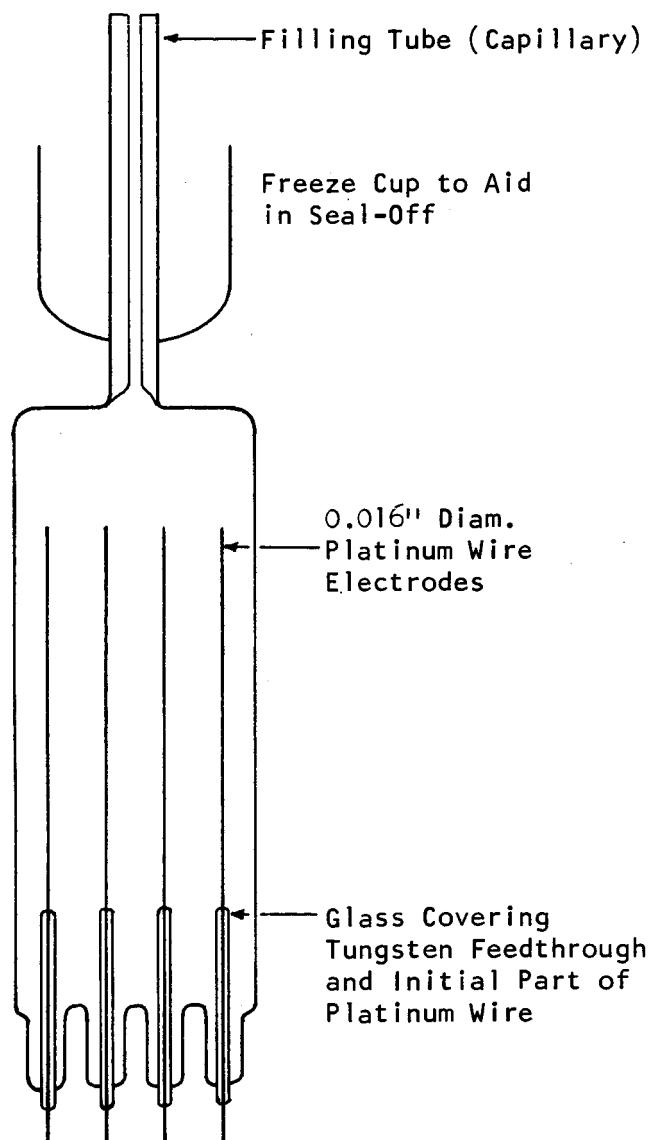


Figure 1. ELECTROPLATING CELL

In some cells two additional electrodes have been brought in through the top of the cell.

In some cells the cathodes have been cut off flush with the feedthrough glass.

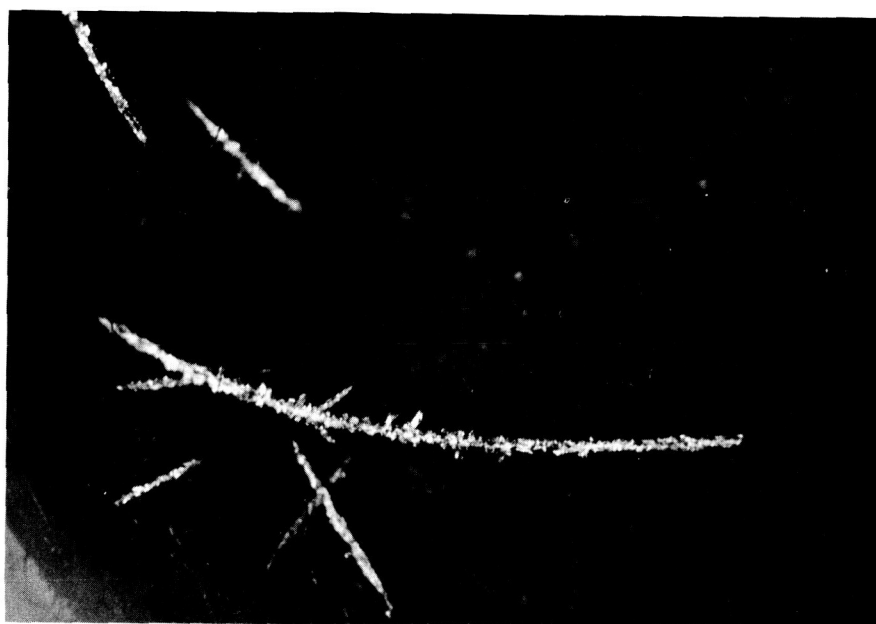


Figure 3. Photograph of Whiskers Deposited in Cell E13 from  $\text{AgNO}_3/\text{NH}_3$  Solution at  $140^\circ\text{C}$ . Length of longest whisker is about 5 mm.



Figure 2. Photograph of the Whiskers Deposited on End of Pt Cathode in Cell E8 From  $\text{AgNO}_3/\text{NH}_3$  Solution at  $140^\circ\text{C}$ .

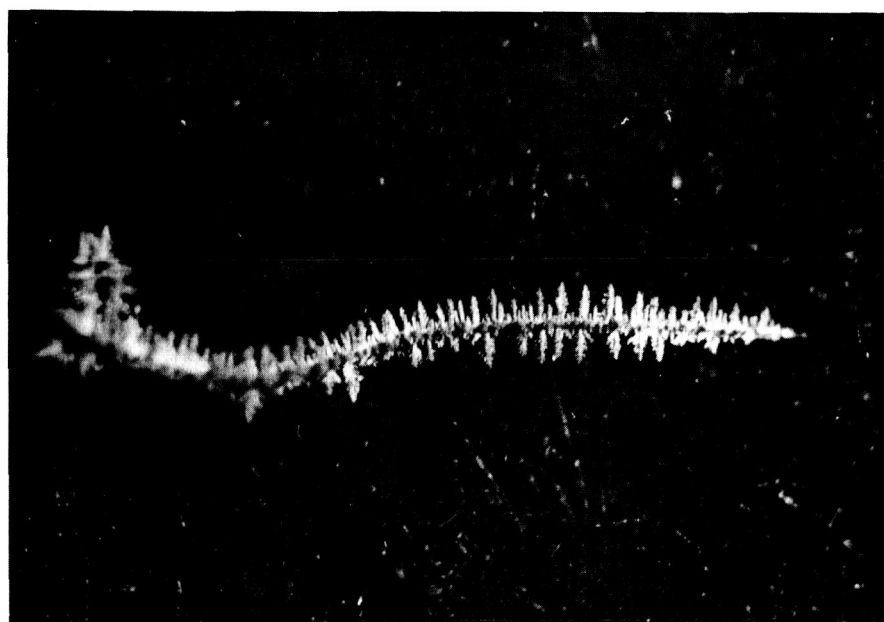


Figure 4. Photograph of a Tree Grown From Gaseous  $\text{AgNO}_3/\text{NH}_3$  Solution at  $141^\circ\text{C}$  in Cell E14. The length of the tree is about 6.5 mm.

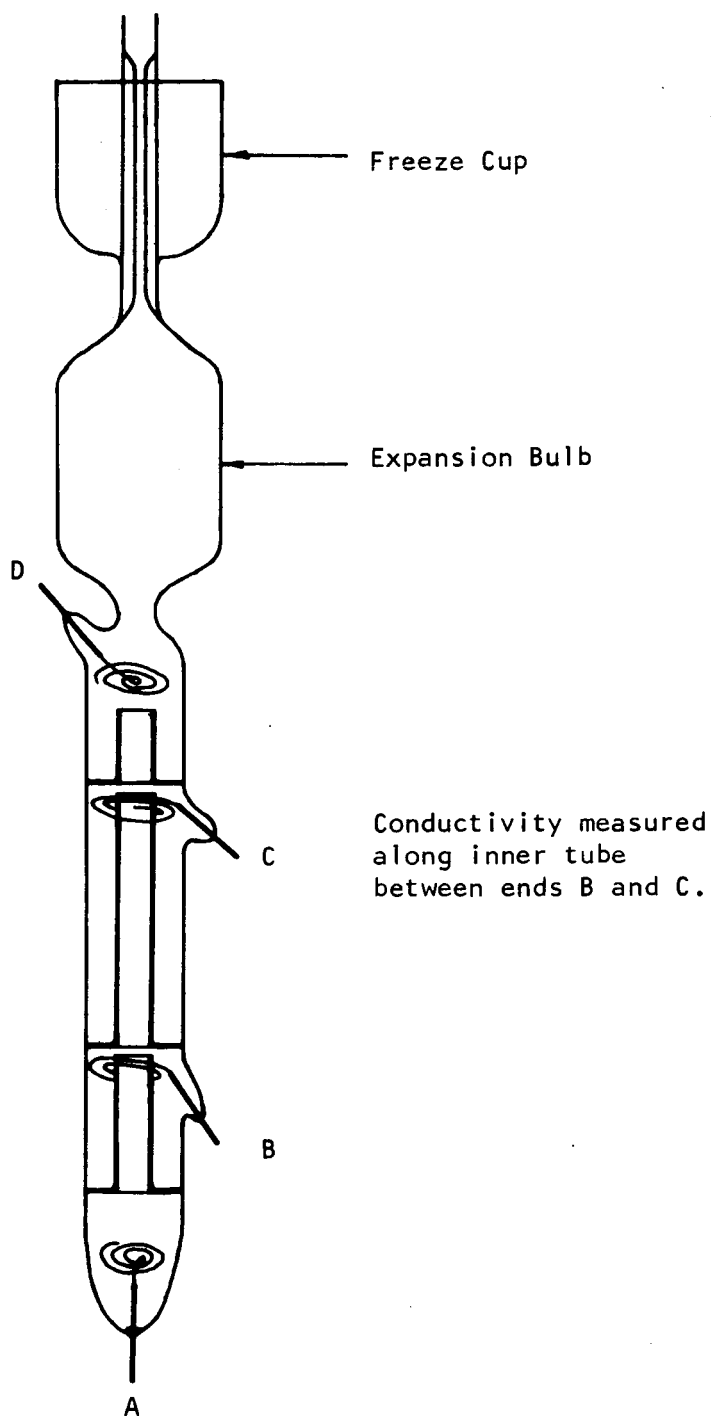


Figure 5. Conductivity Cell for  $\text{AgNO}_3/\text{NH}_3$   
 Cell volume approx. 30 cc.  
 Electrodes are coiled 0.016" diam. Ag wire.  
 A and D are working electrodes.  
 B and C are emf measuring electrodes.

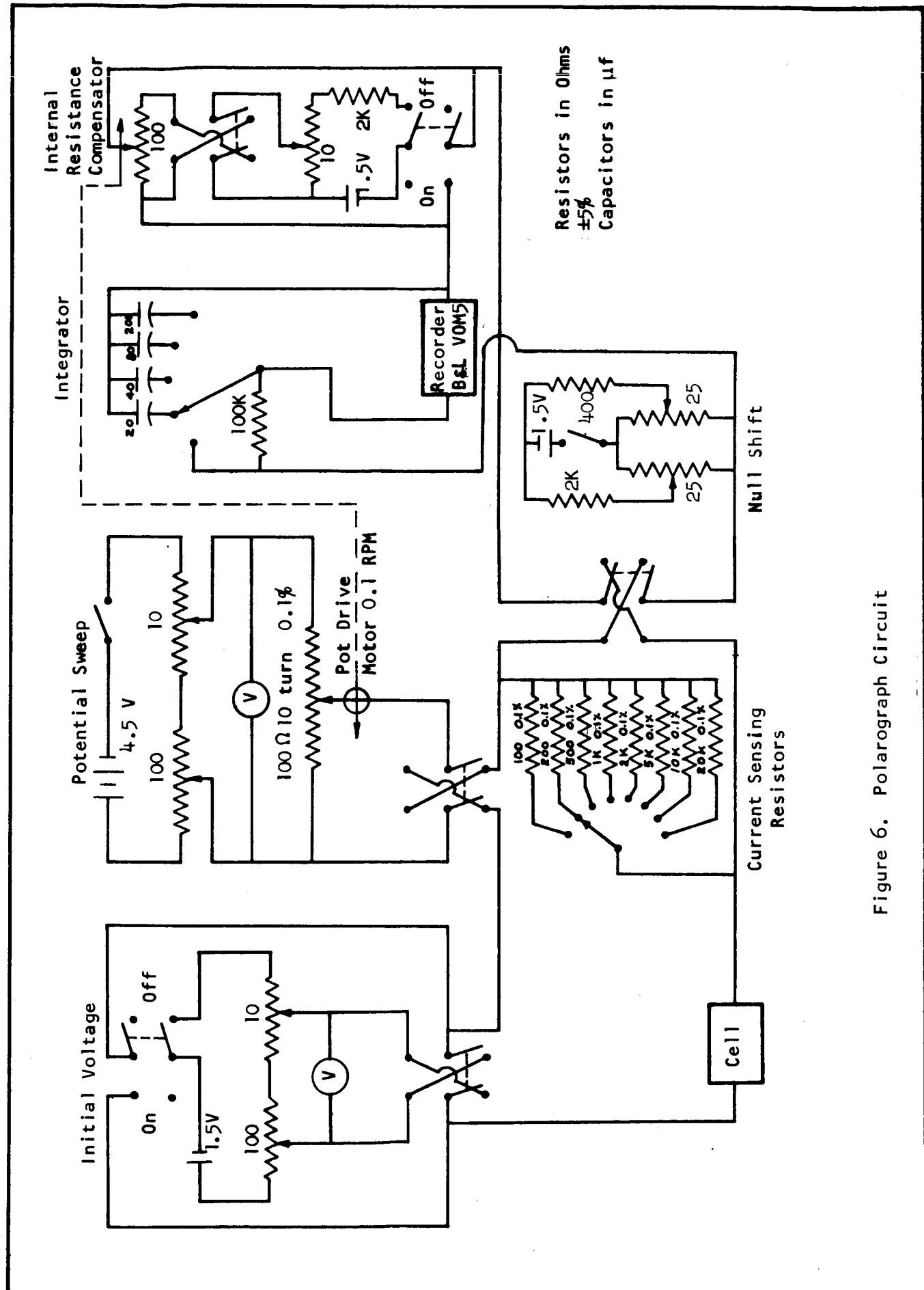


Figure 6. Polarograph Circuit